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ENONE FORMATION FROM ALLYL β-KETO ESTERS, ALKENYL ALLYL CARBONATES, SILYL ENOL ETHERS, AND ENOL ACETATES BY THE PHOSPHINE-FREE PALLADIUM CATALYST

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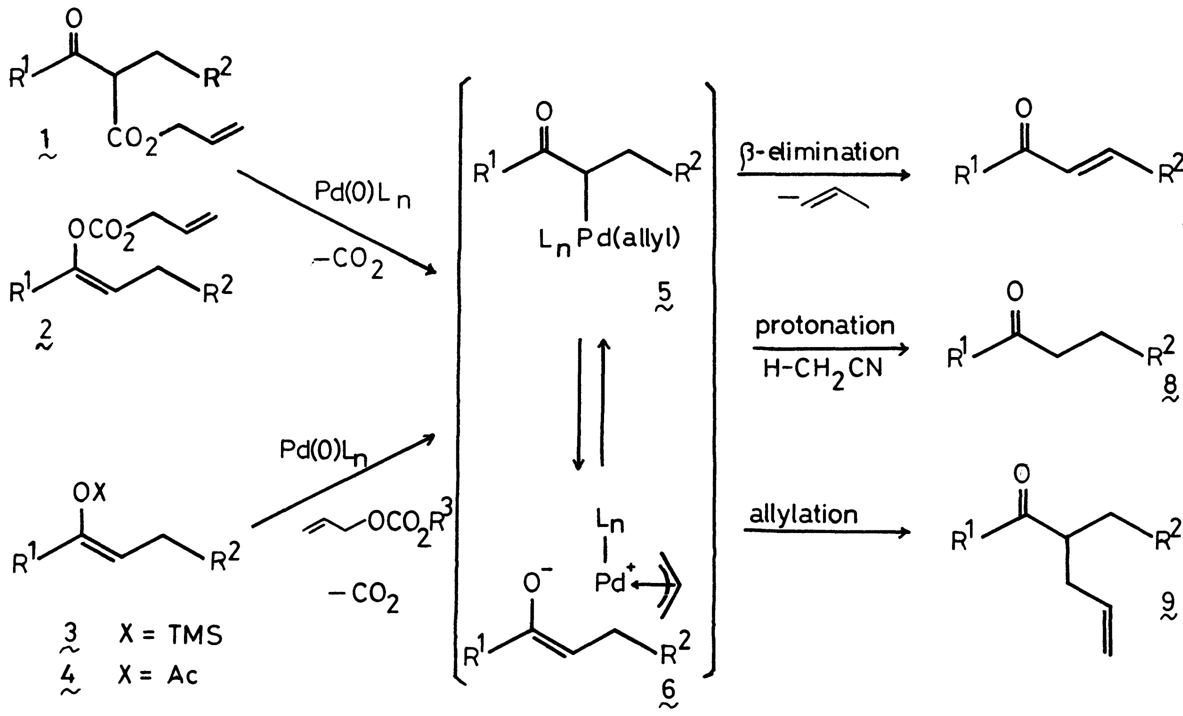
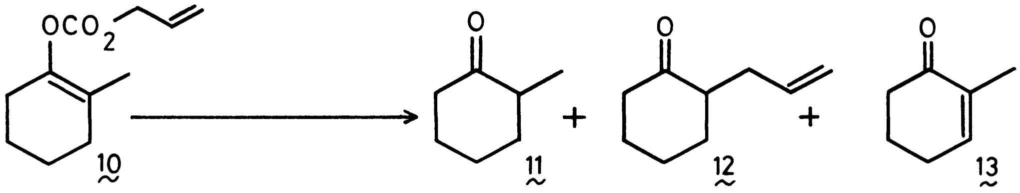
The effect of phosphine ligands on the palladium catalyzed enone formation from allyl β-keto esters, alkenyl allyl carbonates, silyl enol ethers, and enol acetates has been reinvestigated, and clean enone formation was observed by a phosphine-free palladium catalyst.

We have found the palladium-catalyzed enone formation from allyl β-keto esters **1**,[1] alkenyl allyl carbonates **2**,[2] silyl enol ethers **3**,[3] and enol acetates **4**,[4] which proceeds by the β-elimination of allylpalladium enolate complexes **5** or **6** as the common intermediates. These reactions are convenient and simple methods for enone and enal syntheses. However, three competitive reactions are possible from the allylpalladium enolate complex **5** or **6**, namely β-elimination, protonation, and allylation as shown below.



To control the selectivity of these reactions, we found that the selection of solvent and ligand is crucial. For the β-elimination, nitriles are the best solvents. In other solvents, allylation takes place predominantly. As for the ligand, we observed that diphenylphosphinoethane (dppe) is the most active one. Thus in most cases, enal and enone formation proceeds smoothly in MeCN using dppe to give satisfactory yields of enones and enals as reported in the previous communications.[1-3] However, with some ketones, particulary cyclopentanones, the reactions were not selective, and α-allyl ketones **9** and saturated ketones **8** were obtained as major products. In our effort to improve the selectivity of the enone formation, we found very crucial effect of the molar ratios of phosphine/palladium. As shown in Table 1, the crucial effect of the molar ratio on the allylation and β-elimination in the reaction of 1-cyclohexenyl allyl carbonate (**10**) is observed. Even in MeCN and using dppe, allylation was observed when the molar ratio of phosphine/palladium was above 1.5. On the other hand, the enone formation becomes predominant when the molar ratio becomes lower than 1. Surprisingly, we found that the enone formation proceeds cleanly even in the absence of phosphine ligand (entries 5 and 6).

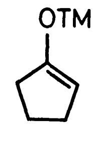
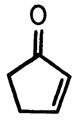
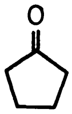
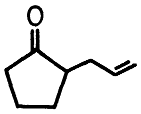
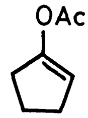
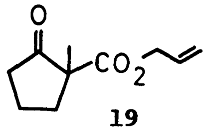
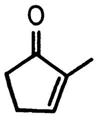
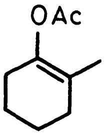
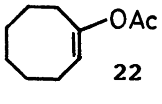
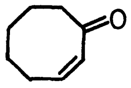
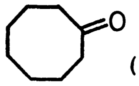
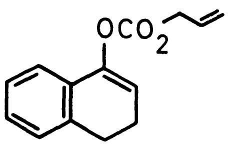
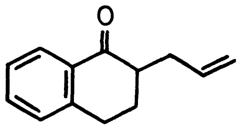
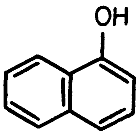
Table 1. Effect of Solvent and Ligand[a)]

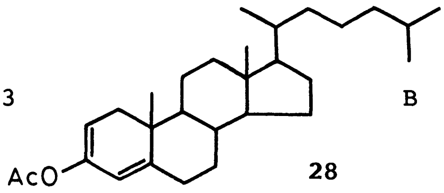
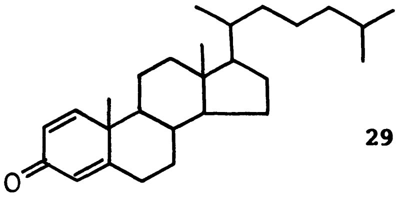
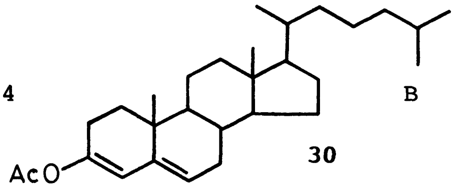
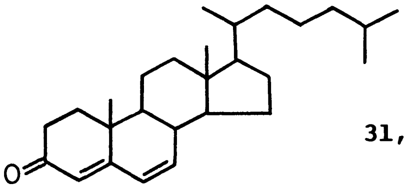


Run	Catalyst	Phosphine	Phosphine/Palladium Molar Ratio	Solvent	Yield[b)]/% 11	12	13
1[c)]	$Pd(OAc)_2$	none	-	THF	0	0	0
2[d)]				THF-TMEDA	0	0	0
3				Pyridine	6	0	17
4				Et_3N	21	12	15
5				MeCN	1	0	98
6	DBA-Pd[e)]	none	-	MeCN	3	0	97
7	$Pd(OAc)_2$	PPh_3	0.54/1	MeCN	1	0	98
8			1.30/1	MeCN	0	5	95
9			1.70/1	MeCN	3	63	34
10	$Pd(OAc)_2$	dppe	0.5/1	MeCN	2	0	86
11			1/1	MeCN	1	0	99
12			2/1	MeCN	4	57	38

a) The reactions were carried out using Pd catalyst (0.1 mmol), **10** (1.0 mmol), dry solvent (5 cm^3) at 80 °C under argon. b) Yields by GLC analyses. c) Reaction at 65 °C. d) Reaction at 65 °C using THF (4 cm^3), TMEDA (1 cm^3).
e) $Pd_2(dba)_3.CHCl_3$.

Table 2. Preparation of Various enones[a,d)]

Run	Substrate	Catalyst[b)]	Solvent	Product, Yield[c)]
1	 **14**	A	MeCN	 **15** (12%)  **16** (72%)  **17** (16%)
2	**14**	A	PhCN	**15** (69%) **16** (0%) **17** (31%)
3	**14**	B	MeCN	**15** (81%) **16** (12%) **17** (0%)
4	 **18**	A	PhCN	**15** (59%) **16** (0%) **17** (12%)
5	**18**	B	MeCN	**15** (100%)
6	 **19**	B	MeCN	 **20** (85%)
7	 **21**	A	MeCN	**13** (9%) **12** (91%)
8	**21**	B	MeCN	**13** (90%) **12** (0%)
9	 **22**	A	MeCN	 **23** (20%)  **24** (80%)
10	**22**	B	MeCN	**23**, 73%
11		A	MeCN	 **26**, 85%
12	**25**	B	MeCN	 **27**, 81%

13	 28	B	MeCN	 **29**, 69%
14	 30	B	MeCN	 **31**, 78%

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a) Reaction of **14**; silyl enol ether (1.0 mmol), allyl methyl carbonate (2.0 mmol), Pd catalyst A or B (0.1 mmol), MeCN (5 cm^3), 80 °C. Reaction of **18**, **21**, **22**, **28**, **30**; enol acetate (1.0 mmol), allyl methyl carbonate (2.0 mmol), Pd catalyst A or B (0.1 mmol), Bu_3SnOMe (0.2 mmol), MeCN (5 cm^3), 80 °C. Reaction of **19**, **25**; allyl β-keto ester or alkenyl allyl carbonate (1.0 mmol), Pd catalyst A or B (0.1 mmol), MeCN (5 cm^3), 80 °C. For detail, see Refs. 1-3. b) Catalyst A $Pd(OAc)_2$-dppe catalyst, (P/Pd = 1/1) see Refs. 1-3. Catalyst B phosphine-free catalyst. c) Isolated yields, GLC yields in parenthesis. d) All products were identified by NMR and IR analyses. **12**, **13**, **15**, **16**, **17**, **20**, **23**, and **24** were also identified by TLC and GLC analyses with the authentic samples. **27** mp 94-95 °C, **29** mp 110-112 °C (lit,4) 110-112 °C) λ_{MAX}^{EtOH} 246 nm (lit,4) 245 nm), **31** mp 80-82 °C (lit, 4) 80-81.5 °C) λ_{MAX}^{EtOH} 284 nm (lit,4) 284 nm).

In Table 2, we compared results of the reactions carried out in the presence and absence of the phosphine ligand. Enones were obtained cleanly by the phosphine-free palladium catalyst.

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References

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3) J. Tsuji, I. Minami, and I. Shimizu, Tetrahedron Lett., 24, 5635 and 5639 (1983).
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